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(54) METHOD AND AN APPARATUS FOR SEPARATING AND FIXING THE COMPONENTS OF A MIXED FLUID SAMPLE

(71) We, SHIMAZU SEISAKUSHO LTD., of No. 378, Ichinofunairi-Cho, Kawaramachidori Nijyosagaru, Nakakyo-ku, Kyoto, Japan, a Japanese Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method and an apparatus for separating a mixed sample of gas, vapour, or liquid into its components and fixing said components in a concentrated condition and, in particular, to a method and an apparatus for fixing the separated components in the concentrated condition after they have been separated by means of a fractionating device such as a chromatograph.

Generally, when analyzing a sample by means of a mass spectrometer, infra-red spectrometer and the like, it is difficult to cary out qualitative and quantitative analysis as the shape of the spectrogram becomes complicated when the sample is in a mixed condition. It is difficult to introduce a large amount of sample at a time into a mass spectrometer, and only a little sample can be handled. Thus, if the concentration of the sample component is low, sufficient accuracy is not obtained due to lack of sensitivity of the spectrometer. Thus, in order to use a mass spectrometer efficiently, it is desirable to separate the sample into its components as much as possible and to introduce the components into the spectrometer in as concentrated a condition as possible. The chromatographic method is commonly employed for separating a mixed sample including a plurality of components. In chromatography the separated components are diluted with a carrier fluid because the sample is differentially migrated in a column with a carrier fluid, and it is undesirable to introduce the components as they are into the mass spectrometer. The peak width of each separated component generally shows some spread in chromatography, due to the diffusion of the components because they are in an activated condition, and this speed imposes a limit on the concentration which can be attained for each component.

One object of the present invention is to provide a method and an apparatus for separating a mixed fluid sample into its components and trapping the separated components in as concentrated a condition as possible so as to be able to introduce those separated components into a spectrometer such as a mass spectrometer.

According to one aspect of this invention there is provided a method of concentrating and trapping the components of a mixed fluid sample prior to elution or other removal of the trapped components comprising the steps of introducing the sample into a column having a stationary phase for separating the sample therein, providing a temperature gradient decreasing in the direction of the fluid flow through the column, and fixing each component in a concentrated condition at the position in the column appropriate to its composition at the time when the components are separated.

According to another aspect of this inven-

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tion there is provided a method of concentrating and traping the components of a mixed fluid sample comprising the steps of connecting a separating column having a stationary phase to the sample component outlet pipe of the main separating column of a chromatograph, and providing the first mentioned separating column with a temperature gradient decreasing from its inlet to its outlet, whereby the components separated by the chromatograph are fixed to the first mentioned column in a concentrated condition.

According to a further aspect of this invention there is provided apparatus for concentrating and trapping the components of a mixed fluid sample comprising a column having a stationary phase for separating the sample therein, a pressure difference means for providing a pressure difference between the ends of the column, a sample introducing means for introducing a mixed fluid sample containing a plurality of components into the high pressure side of said column, and a temperature gradient device for providing a temperature gradient over a portion or the whole of said column decreasing towards the low pressure end of the column so that the components of the fluid sample are separately fixed to the column.

According to yet another aspect of this invention there is provided apparatus for concentrating and trapping the components of a mixed fluid sample separated by a chromatograph having a sample separating column, the apparatus comprising a further separating column including means for providing a temperature gradient decreasing from its inlet to its outlet, said second column being connected to the outlet of the chromatograph so that the components of the sample separated by the chromatograph are fixed separately at different positions in said second column in a concentrated condition.

The fluid sample may be a gas or liquid sample.

Embodiments of this invention will now be described, by way of example only, with reference to to the accompanying drawings of which:—

Fig. 1 is a schematic diagram of one embodiment of this invention,

Figs. 2 and 3 are explanatory graphs illustrating the operation of this embodiment,

Figs. 4, 5 and 6 are more detailed diagrams of alternative separation fixing devices 4, the device 4 being part of the embodiment shown in Fig. 1;

Fig. 7a is a schematic diagram of another embodiment of this invention, this embodiment incorporating a gas chromatograph;

Fig. 7b is a chromatogram of the outlet gas of the gas chromatograph of Fig. 7a;

Fig. 7c is a graph showing the concentration and distribution of the trapped components after passing through the separation fixing device of Fig. 7a; and

Fig. 8 is a view partly in section showing a device for eluting the components fixed by the separation fixing device of Fig. 7a.

Referring to Fig. 1, the reference numeral 1 denotes a device for introducing a mixed sample containing a plurality of components and 2 indicates a column having therein a stationary phase such as a column used in gas/chromatography the cross section of which may have various shapes such as a circle, a square and the like. The stationary phase employed may be a solid phase such as alumina, charcoal and silica gel, or a liquid phase such as silicone oil coated on or impregnated into the supporting medium. The reference numeral 3 indicates a thermostatically controlled bath, 4 a temperature gradient device, and 5 a high quality spectrometer such as a mass spectrometer. The numeral 6 indicates a flow path changing cock, 7 a movable heater, 8 a carrier gas cylinder of helium, neon or the like, and 9 a resistance pipe being a pipe of small internal diameter offering resistance to the flow of fluid therethrough. The numeral 10 indicates a flow stopcock, 11 stripping column, 12 a carrier gas flow adjuster, 13 two valves and 14 a pressure gauge.

The sample components in a mobile phase are separated by means of adsorption or partition within a stationary phase in a column, the components remaining on the inner wall of the column or in the stationary phase being fixed on account of the temperature variation. The fixed components are then removed in a fluid or gas condition through elution or flowing.

The sample introduced by the sample introducing device 1 (Fig. 1) is separated into its components in the column 2, and the separated components are fixed on the stationary phase on the inner wall of the column 2 at different positions along its length. This fixing is carried out by giving a temperature gradient to the column 2.

The linear velocity v of each of the sample components is given by the following formula:

$$v = \frac{u}{1 + k \cdot \frac{V_l}{V_g}} \qquad (1)$$

wherein u is a linear velocity of a carrier gas or developer, k is a partition coefficient, and $\frac{V_l}{V_g}$ is a ratio of the stationary phase area to the mobile phase area of the separated components in cross section. The partition coefficient k is given by the following formula:—

$$k = C \exp \frac{(-\Delta H)}{RT} \qquad (2)$$

wherein C is a proportion coefficient, R is the gas constant, T is the absolute temperature and ΔH is the latent heat when 1 mol of the sample components is sorbed into the stationary phase and is ordinarily negative. The partition coefficient k increases exponentially as the temperature decreases.

Fig. 2 is a graph showing the relation between k and T^{-1} for three components A, B, and C, which shows that the increase of k as the temperature decreases differs for A, B, and C. As seen from Fig. 2 the value of the partition coefficient k of each of the components A, B and C is made extremely large at each of the temperatures T_A, T_B and T_C corresponding to the respective components A, B and C. The linear velocities v_A, v_B and v_C respectively of the components A, B and C become very small at the temperatures of T_A, T_B and T_C respectively as is apparent from formula (1).

In the separation fixing device, the sample is separated in the column 2 and the separated components substantially cease to flow at said temperatures T_A, T_B and T_C, respectively, the temperature gradient device 4 giving a decreasing temperature gradient to the column 2 from its inlet to its outlet. Fig. 3 is a graph showing the temperature gradient in the column 2. The components A, B and C are fixed at the positions a, b and c respectively in the column 2 corresponding to the temperatures T_A, T_B and T_C respectively.

The temperature gradient of the column 2 may be applied to the whole of the column 2, but in case of the device shown in Figure 1 the portion of the column 2a is maintained at a constant temperature and the portion 2b of the column 2 connected to said portion 2a of the column 2 has the temperature gradient applied to it. Thus, the sample is separated in the portion 2a of said column in the thermostat bath 3 and is fixed in the portion 2b of said column 2 by the temperature gradient device 4. In this case, the separated components have some deviation in the mobile phase, but as the temperature zone during fixing is defined, this results in concentration.

In order to introduce the fixed components from the said column portion 2b into the spectrometer 5 after fixing, the temperature grdient producing operation of the temperature gradient device 4 is stopped by switching a temperature controlling device 4a and a cooling device (see Figs. 4 and 6) is operated which cools the column portion 2b to an appropriate temperature and thus stabilizes the said fixing. Then the change valve 6 is rotated by 90° in the counterclockwise direction for analysis metering and a heater 7 (the heater-block 21 in Fig. 4 may be used) surrounding the column portion 2b is gradually moved from its outlet in the direction of the arrow. In this way elution of the separated components fixed to the column portion 2b is gradually carried out at the low pressure side of the outlet. When the spectrometer 5 is a mass spectrometer, the negative pressure is utilized for separate flowing out of the components. The sample elution operation which is carried out by moving the components adsorbed on the filler on the inner wall of the column portion 2b with the advancing of the heater 7 can also be carried out by introducing a small amount of carrier gas from the carrier gas cylinder 3 through the resistance pipe 9 and the stop cock 10. If one of the stationary phase components other than components of the mixture to be separated adsorbed in the column flow out when the column portion 2b is heated with the heater 7, a stripping column 11 for removing the liquid phase should be connected in the line to the spectrometer to prevent such stationary phase components from being introduced into the spectrometer.

Since the higher the temperature gradient at the left edge of the moving heater 7, the greater is the concentration effect without failure of separation, it is desirable to dispose a cooling plate or an insulating member 7a at the front of the heater 7 in order to prevent the heat from being transmitted through the column portion 2b in the direction of the arrow. (If the heater 7 transmitted forward in the direction of the arrow, it is possible that the components fixed in front of the heater 7 may be caused to flow out at the wrong time).

Although in the arrangement shown in Fig. 1 the column portion 2b having the separated components fixed thereto is mounted to the rest of the separation fixing device when the fixed components are removed, the heater and the column portion 2b to which the components are fixed may be separable from the separation fixing device and separated therefrom when the fixed components are removed by the heater 7.

The separation fixing device just described is a device which carries out fixing of the components separated by the device as well as sample introducing in the manner of an ordinary chromatograph and effecting separation in a column.

While the temperature gradient is applied the advancing velocity of each of the separated components in the device becomes zero at a position on the column portion 2b where the temperature is peculiar to that separated component and that component is fixed to the column portion 2b at that position. Although the fixed components may be present in extremely small quantities, they are fixed concentrated to a high density because each com-

ponent is fixed in an extremely narrow zone, and the efficiency of the rate of adsorption at which one component is adsorbed at one position in the column is near to 100%.

Referring to Fig. 4, which shows details of the temperature gradient device 4, the reference numeral 20 denotes a cylindrical heat conductor block of a material such as aluminium and having at its centre a bore through which the column portion 2b passes, 21 a heating coil element for heating the end of the said conductor block 20 at the high pressure side of the column portion 2b, and 22 and 23 respectively a heating coil element and cooling coil for controlling the temperature at the other end of the said block 20 that is the low pressure side of the column portion 25, for keeping that end at a definite temeprature lower than the said high pressure side. It will be appreciated that the net heating effect at the low pressure end of portion 2b will be the difference between the heat output element 22 and the heat extracted by cooling coil 23. The numeral 24 denotes an insulating wall for preventing the surface temperature of the said block 20 from varying with the outside temperature so that the temperature within the bore in the block is maintained at a constant value, 25 a heating current controlling device for the said heating coil element 21 for maintaining the temperature at the high pressure end of the column portion 2b at a definite temperature such as 200°C, 26 a heating current controlling device for the heating coil 22 at the low pressure end of the column portion 2b for maintaining the temperature at the lower pressure end of the column portion 2b at a definite temperature such as 30°C, and 27 an electric supply for the said heating current controlling devices 25 and 26. Although it is not shown in the drawing, because the temperature difference between the two ends of the column portion 2b is required to be strictly regulated to a definite value a temperature detecting element or the like is disposed at each end of the column or block and the said controlling devices are automatically controlled in accordance with the temperature detected by these elements so that the temperatures at the high pressure and lower pressure ends of the column portion 2b are regulated. By controlling the temepratures at the ends of the said block 20 and maintaining these temperatures at different values, heat is conducted from the high pressure end to the lower pressure end of the column portion 2b through the said aluminium block 20, so that the column portion 2b is provided with a linear temperature gradient.

The space between the wall 24 and the block 20 is filled with a cooling medium when the column portion 2b has to be cooled uniformly. The reference numeral 28 indicates a device for controlling the temperature within the bath 24, 29 a cooling medium introducing device, and 30 a valve for said cooling medium introducing device 29.

Referring to Fig. 5 which shows an alternative temperature gradient device 4, a plurality of band heaters h_1, h_2, h_3, . . . h_n are disposed around the column portion 2b. By suppling the said band heaters with increasing voltages from an end to the other end from an electric supply P a desired temperature gradient is provided for the column portion 2b.

Referring to Fig. 6 which shows a further alternative temperature gradient device 4, a number of thermoelements 29′ are arranged around the column 2b. By suppling increasing current to the thermoelements from one end to the other of the portion 2b from a source 31, a desired temperature gradient is provided for the column portion 2b. The reference numeral 32 denotes a mounting block for the said thermoelements 29′ and 33 denotes a cooling medium circulating pipe for cooling the said column portion 2b. The thermoelements 29′ can be used as cooling elements by changing the supply current polarity after being used as heating devices for providing a temperature gradient for the said column portion 2b and the column portion 2b can be cooled in this way (i.e. they can be used for stabilizing the fixed components). Moreover, said thermoelements 29′ may be used to cause each of the fixed components to flow separately by shifting the time of heat generation by the individual thermoelements by energising sequentially all the thermoelements beginning with the thermoelement 29′ at the outlet end of the column portion 2b.

Various types of temperature of gradient producing devices other than those already described, may be employed such as a column with an electric heating wire wound thereon in a spiral or zigzag with varying pitch and a device using a fiuid heating medium.

An exemplary process using the arrangement shown in Figure 4 was as follows.

A stainless steel column 2 of 3 mm inside diameter and 4 mm outside diameter, was filled with a fire brick powder supporting medium of size 60—80 mesh impregnated with 15% SE 30 (the commercial name of a methyl silicone rubber made by U.S. General Electric Co.) as a stationary phase. A sample of fatty acid methyl ester having various components having different numbers of carbon atoms e.g. C_8, C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, was introduced into the column through which the sample flowed at a rate of 100 cc/min from the inlet to the outlet. A helium gas carrier was used so that a mobile phase was formed in the column creating a pressure difference between the two ends of the column 2. The column portion 2b was inserted into an aluminium block of 20 to 50

cm in length disposed in the thermostatically controlled bath 24 and the temepratures at the inlet of the column was 200°C, and at the outlet, 30°C, with a linear temperature gradient therebetween, and this condition was maintained for about 30 minutes. The valve 13 was then closed to stop the flow of the carrier gas and the heating devices 21 and 22 at the ends of the column portion 2b were de-energised. Air at normal temperature was then introduced into the cylinder 24 from the cooling medium introducing device 29 (the aluminium block 20 was previously removed) andthe column portion 2b was maintained at a normal temperature, the component in the sample having most carbon atoms (methyl stearate C_{18}) being fixed to the part of the column portion 2b nearest its inlet. The component having the next highest number of carbon atoms (palmitates . . . C_{16}) was fixed to the portion 2b adjacent to the said part nearest to the inlet. Similarly those components having less carbon atoms (C_{14}, C_{12} . . .) were fixed, in order, to the column portion 2b at equal intervals along it in the longitudinal direction from the inlet and the component having the least number of carbon atoms (C_8) was fixed in a stable manner and in a concentrated condition to the portion 2b at the position nearest to the outlet of the column portion 2b.

The valve 10 was then opened to allow a small amount of helium carrier gas at a rate of about 10 cc/min enter the column portion 2b to which said sample components were separately fixed and a pressure difference between the ends of the portion 2b was caused. The heater 7, heated to about 250°C, was moved gradually from the low pressure side to the high pressure side of the column portion 2b and the fixed components were eluted out. The component having lowest number of carbon atoms (C_8) was eluted first, the component having the next higher number (C_{10}) was eluted second in a high concentration in the carrier gas, and the other components were eluted sequentially. The component having the greatest number of carbon atoms (C_{18}) was eluted at the end. These components were in sufficient concentration to be introduced into the mass spectrometer.

Referring now to Fig. 7a which shows an embodiment of the present invention incorporating a gas chromatograph, the reference letter T denotes a carrier gas source, and G represents the gas chromatograph which comprises a sample introducing compartment S, a main column C_L, a detector D and a recorder R. The reference letter F denotes a separate trapping device and the letter M denotes a mass spectrometer as shown in Fig. 1.

The components separated by a chromatographic device flow out having various peak widths. The peak width, that is, the time from the start of flow out to its end, is related to its retention time. Thus if the peak width is large, the concentration decreases and the peak becomes lower with large spread. Further the density of the separated components is also low, but each component is fixed to the column in a concentrated condition in the said trapping device F. The separated components having a distribution as shown in Fig. 7b at the said detector D become as shown in Fig. 7c at the outlet of the said device F. The components thus fixed may be taken out by splitting or breaking the column, but it is more desirable to take out the fixed components by the following method.

Referring now to Fig. 8 which illustrates a device for eluting the separated and fixed components, a carrier gas is introduced in the direction of the arrow into the column 2b. (In Fig. 8 the column containing the components is denoted by the reference 2b). A heater 40 having a slit 41 which allows the tube portion 42 to pass therethrough is movable from the outlet side to the inlet side of said column 2b. In order to clarify the boundary of the heating portion and the un-heated portion, a cooling ring 44 is mounted to the column prior to the heater 40. The cooling ring 44 is cooled with a thermoelement or with a cooling medium. The reference numeral 43 denotes an insulating member for insulation between the said cooling ring 44 and the said heater 40. The thickness of the insulating member 43 should be as thin as possible e.g. 0.2 mm. The reference numeral 45 denotes a stripping column for removing impurities from said eluted gas. (A stripping column is a short chromatographic column conventionally used in a gas chromatograph for the adsorption of the vapour of the substance constituting the liquid phase).

When the heater 40 is moved in the direction of the arrow, the component fixed in the column 2b is eluted in the gas phase and is carried out of the column with the carrier gas. The heater 40 extends up to the end of the column so as to keep the eluted components in a gaseous state.

It is not necessary to control strictly the temperature of the heater 40 but it is desirable to provide the heater with a temperature gradient increasing towards the rear end. The cooling ring 44 can be made long enough to hold in a stable manner the fixed components in the unheated portions.

The velocity of the heater 40 is related to the final concentration of the components. For instance, if it takes one hour to separate all the components and the components are fixed the components and the components are fixed to a column 10 cm long in a gas chromatograph, it takes 10 minutes to elute all the components when the heater 40 is moved at the rate of 1 cm/min and this results in a con-

centration of six times. When using this trapping device with a mass spectrometer the linear velocity in the column is fixed according to the rate of flow capable of being taken into the spectrometer. As the column is set to provide the maximum efficiency, the inner pressure of the column is different from the inner pressure of the chromatographic device. For instance, the inner pressure of the column 2b may be 7.6 mm Hg (the pressure drop along the column can be neglected).

The pressure at the outlet of the column of a gas chromatograph may be 760 mm Hg. In this case the said six times is multiplied further by 760/7.6=100. The value can be made much larger than the one described above by appropriately selecting the resistance pipe or controlling the pressure controlling device. As is apparent from the above description, the concentration magnification is related to the velocity of the heater and the inner pressure.

The method and apparatus in accordance with the present invention make it possible to concentrate components separated by chromatography so that they have a higher concentration without any loss.

Although the various embodiments were described mainly in connection with gas chromatography and with separate fixing of a gas, this invention is also applicable to liquid chromatography.

The elution device and method described above with reference to Fig. 8 form the subject of our co-pending divisional application No. 33397/68, (Serial No. 1204898) which contains claims is a method of, and apparatus for, eluting the components of a mixed fluid sample at different positions on the stationary phase of a column.

WHAT WE CLAIM IS:—

1. A method of concentrating and trapping the components of a mixed fluid sample to elution or other removal of the trapped components comprising the steps of introducing the sample into a column having a stationary phase for separating the sample therein, providing a temperature gradient decreasing in the direction of the fluid flow through the column, and fixing each component in a concentrated condition at the position in the column appropriate to its composition at the time when the components are separated.

2. A method as claimed in Claim 1, wherein the initial portion of the column is thermostatically maintained at a fixed temperature and the remainder of the column is profixed with a decreasing temperature gradient.

3. A method as claimed in Claim 1 or Claim 2, including elution by the steps of heating a zone of the said components while displacing or extending the heated zone along a length of the column in a direction from the outlet end towards the inlet end of said length, and providing a pressure gradient decreasing in the opposite direction, whereby the components flow out of the column successively in a concentrated form.

4. A method as claimed in Claim 3, where- i nthe heating of the said zone of the column is effected by a heater which embraces the column and which is moved from the outlet of the column towards the inlet.

5. A method as claimed in any preceding Claim, wherein after the components are fixed in the column, the column is cooled.

6. A method of concentrating and trapping the components of a mixed fluid sample comprising the steps of connecting a separating column having a stationary phase to the sample component outlet pipe of a main separating column of a chromatograph, and providing the first-mentioned separating column with a temperature gradient decreasing from its inlet to its outlet, whereby the components separated by the chromatograph are fixed to the first-mentioned column in a concentrated condition.

7. Apparatus for concentrating and trapping the components of a mixed fluid sample comprising a column having a stationary phase for separating the sample therein, a pressure difference means for providing a pressure difference between the ends of the column, a sample introducing means for introducing a mixed fluid sample containing a plurality of components into the high pressure side of said column, and a temperature gradient device for providing a temperature gradient over a portion or the whole of said column decreasing towards the low pressure end of the column so that the components of the fluid sample are separately fixed to the column.

8. Apparatus as claimed in Claim 7, wherein said pressure difference means comprises means for supplying a carrier fluid which carries the sample from one end to the other end of said column.

9. Apparatus as claimed in Claim 7 or Claim 8, wherein said temperature gradient device comprises a heat conductor block disposed around said column, and means for keeping the temperature at the ends of said block at defined temperatures.

10. Apparatus as claimed in any of Claims 7 to 9 which comprises means for heating a zone of said column and displacing or extending heated zone along a length of the column in a direction from the outlet of the column towards its inlet, whereby the fixed sample components are successively caused to flow out of the low pressure end of said column in a concentrated condition.

11. Apparatus as claimed in Claim 10 wherein said temperature gradient device acts as said means for heating and has a number of heater elements which are separately energisable.

12. Apparatus as claimed in Claim 10 wherein said means for heating comprises a

heater which embraces the column and which is movable away from the outlet of the column towards the inlet.

13. Apparatus as claimed in any of Claims 7 to 12, which includes means for cooling the column.

14. Apparatus for concentrating and trapping the components of a mixed fluid sample comprising a chromatograph including a sample separating column and a further separating column including means for providing a temperature gradient decreasing from its inlet to its outlet, said second being connected to the outlet of the chromatograph so that the components of the sample separated by the chromatograph are fixed separately at different positions in said second column in a concentrated condition.

15. Apparatus for concentrating and trapping the components of a mixed fluid sample separated by a chromatograph having a sample separating column, the apparatus comprising a further separating column including means for providing a temperature gradient decreasing from its inlet to its outlet, said second column being connected to the outlet of the chromatograph so that the components of the sample separated by the chromatograph are fixed separately at different positions in said second column in a concentrated condition.

16. Apparatus as claimed in Claim 14 or Claim 15, which includes heating means for heating a zone of said further column and displacing or extending the heated zone away from the outlet towards the inlet.

17. A method of concentrating and trapping the components of a mixed fluid sample substantially as hereinbefore described with reference to Figure 1 in association with any of Figures 4 to 6 or to Figures 7a and 8.

18. Apparatus for concentrating and trapping the components of a mixed fluid sample as claimed in claim 7 and substantially as hereinbefore described with reference to Figure 1 in association with any of Figures 4 to 6 or as claimed in Claim 14 and substantially as hereinbefore described with reference to Figures 7a and 8.

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1204897 COMPLETE SPECIFICATION

3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

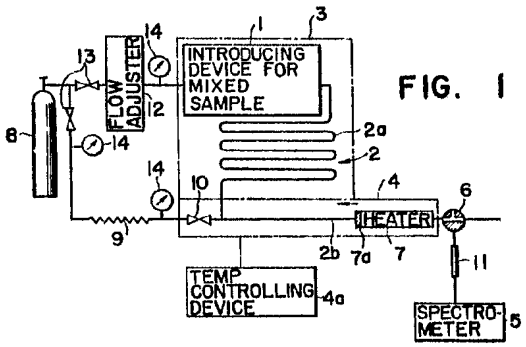

FIG. 1

FIG. 2

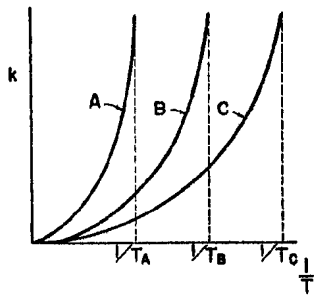

FIG. 3

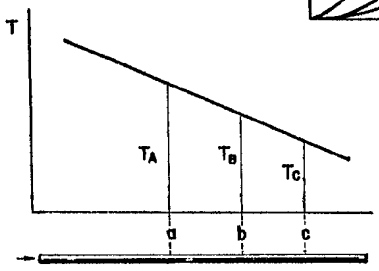

FIG. 4

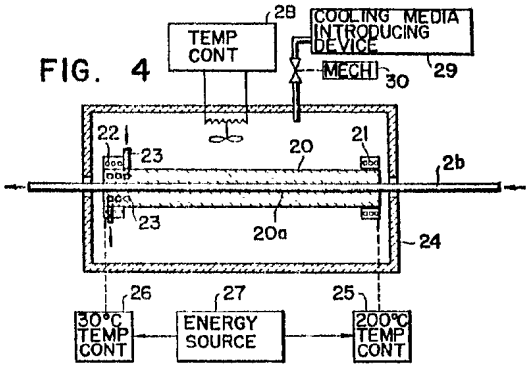

FIG. 5

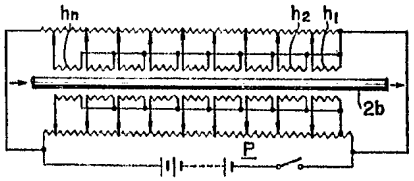

FIG. 6

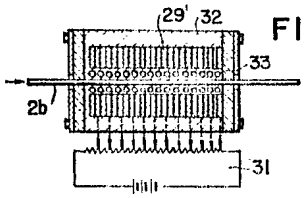

FIG. 7a

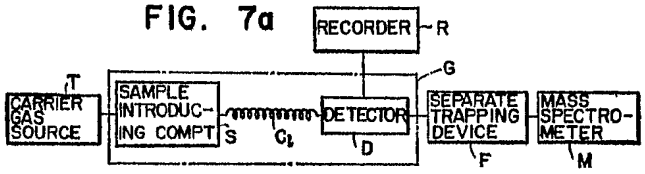

FIG. 7b

FIG. 8

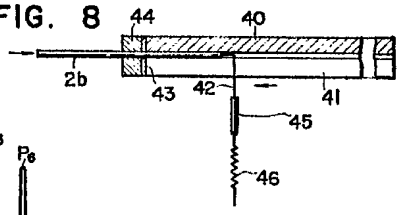

FIG. 7c